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AC-conductivity of lead-bismuth-titanate glasses

D K Burghate* and V S Deogaonkar
P G Department of Physics, Shri Shivaji Science College,
Amravati-444 603, India

(Miss) S V Pakade and S P Yawale
P G Department of Physics, Government Vidarbha Mahavidyalaya,
Amravati-444 604, India

Abstract : The ac-conductivity of five samples of lead-bismuth-titanate glasses have been measured at various temperatures and frequencies. It is observed that, the activation energy for dc-conductivity increases with decrease in PbO concentration at temperature 533K. The ac-conductivity follow the relation $\sigma(\omega) = A\omega^S$ (where A is constant and S is exponent). The values of the exponent (S) has been evaluated from the plot of log $\sigma(\omega)$ *versus* log ω. It is found that the values of S decreases with decrease in PbO composition except for the glass BX1. Existing theories of ac-conduction have been analysed for interpretation of the present results. Values of the density of state at the Fermi level for different compositions of glasses has the order of 10^{20} eV^{-1} cm^{-3} (considering α-electron wave function decay constant equal to 0.9 Å^{-1} evaluated from the log σdc *versus* hopping distance R) which suggest that the conduction is in localized states near the Fermi level. It is observed that the ac-conductivity increases with frequency. The value of exponent (S) has been calculated and was found to be less than 1. The results of ac-conductivity are discussed on the basis of QMT model for the present glass system.

Keywords : Ac-conductivity, lead-bismuth titanate glasses, QMT model

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1. Introduction

The electrical conductivity and dielectric constant are interesting properties which provide important information regarding the conduction mechanism in solids. In the recent years, there has been an increasing interest in the study of electrical, optical and structural properties of oxide glasses, because of their potential applications, such as switching and memory devices, thermistors and semiconductors. The transition metal oxide glasses show semiconducting behaviour, because of transition metal ions. Electrical transport properties of these glasses have been studied by a number of research workers [1-3]. For amorphous materials various types of conduction mechanisms have been suggested by Mott and Davis [1].

The hopping conduction in localized states gives rise to frequency dependent ac-conductivity of semiconducting oxide glasses. Therefore, measurement of ac-conductivity in glasses and other amorphous materials is a powerful experimental method to obtain information about the existence of localized states. Such measurements on chalcogenide glasses have been reported by many research workers [4, 5]. The ac-conductivity at low temperature is almost independent of temperature but shows strong frequency dependence as $\sigma(\omega) \sim A\omega^S$ [3]. The exponent (S) has been reported to be less than unity by Mansingh *et al* [3]. Ac-conductivity of iron-phosphate [6] and tungstan phosphate glasses (3) have already been studied and the data have been analysed in terms of different models such as QMT model and HOB model.

The dependence of ac-conductivity $\sigma(\omega)$ with ω^S, $S < 1$ is found to be a general characteristics for these glasses up to the frequencies of 1 MHz. However, there is an apparent controversy over the nature of the temperature dependence of $\sigma(\omega)$. Some workers [4, 7] have reported a temperature dependent ac-conductivity, whereas others [7,8] have observed temperature independent behaviour of $\sigma(\omega)$ even at frequencies at low as 1 kHz. Burghate *et al* [9] have reported ac-conductivity of lead-bismuth glasses at various temperatures and frequencies. The effect of composition of glasses on ac-conductivity has been discussed.

Pike [10] and Elliott [11] have suggested that ac-conductivity is a phenomenon due to hopping of charge carriers over the barrier, called HOB. This model discussed the frequency and

* Corresponding Author

temperature dependence of conductivity. Various models have been developed to interpret the ac-conductivity results. The models are (i) quantum mechanical tunnelling (QMT) (ii) overlapping polaron tunnelling, (iii) correlated barrier hopping (iv) hopping over the barrier *etc.*

In the present paper, authors have studied the electrical, conductivity of PbO-TiO_2-Bi_2O_3 glasses at three different frequencies 0.1, 1 and 10 kHz in the temperature range 313-673K. Similarly the dc-electrical conductivity is also measured for the same temperature range. The quantum mechanical tunnelling is found to explain the ceconductivity data of the present glasses well.

2. Experimental details

2.1 *Preparation of samples :*

Glass samples under investigation were prepared in the laboratory by mixing appropriate amounts of Bi_2O_3, TiO_2 and PbO (mol %) using Anala-R grade chemicals. A homogeneous mixture of two powders were prepared and fired in a fireclay crucible at 1000 ± 10°C for half an hour in an automatically temperature controlled muffle furnace. The glass samples were then formed by quenching the melt on a steel plate held at room temperature. The X-ray diffractograms of all the glass samples are determined (Figure 1). The absence of peak in the X-ray spectra, confirmed the amorphous nature of glass samples. Samples were then polished by emery paper. A thin conducting silver paint, circular in shape is applied on the opposite sides of the sample for the purpose of electrical measurements. Samples were annealed at 100°C for about two hours to stabilize the contacts and also to remove mechanical stresses. The differential thermal analysis (DTA) of the samples is done in the temperature range 30–570°C in air (Figure 2). The glass transition temperature (Tg) is determined and presented in Table 1.

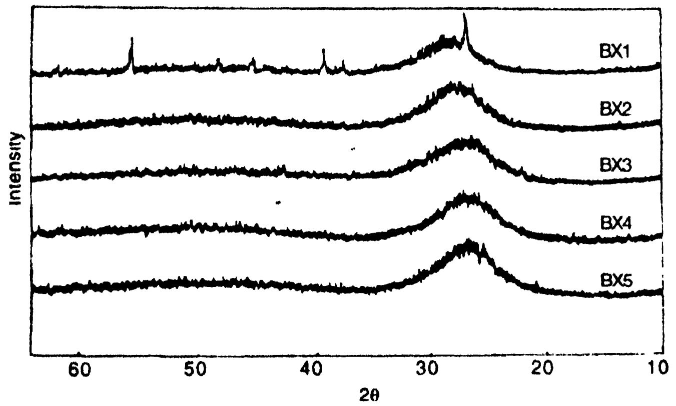

Figure 1. X-ray diffractograms of samples BX1, BX2, BX3, BX4 and BX5

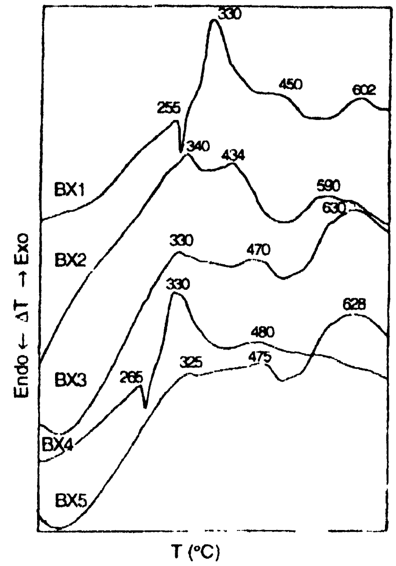

Figure 2. DTA-curves of glass samples, BX1, BX2, BX3, BX4 and BX5

2.2 *Electrical measurements :*

Ac-electrical conductivity of glass samples was measured by finding out the resistance of the sample. The resistance of the glass was measured by voltage drop method given by Kher and Adgaonkar (14) and Yawale and Pakade (15). The voltage measurements across the standard resistance of 1 Meg-ohm was carried out by using ac-microvoltmeter (systronic 411 India) having accuracy ± 1 μV and input impedance 10 Meg-ohm. The ac-resistance of the glasses of various compositions was measured at ac-voltage (IV) in the temperature range 313-673K.

The ac-conductivity was measured at frequencies 100 Hz, 1 kHz and 10 kHz. The reproducibility of the results was checked by making many runs at different times over the entire temperature and frequency range. It was observed that the conductivity behaviour was always the same and the values of conductivity were within ± 2% of error in different runs.

Table 1. Values of $\sigma(\omega)$ of 533K at 10 kHz and exponent S_{exp}

Sample No.	Glass compositions (mol %)			Glass transition temperature (Tg)K	$\sigma(\omega)$ at 533K $(\text{ohm-cm})^{-1}$	Activation energy (eV) at 533K from dc-conductivity	S_{exp} at 543 K
	PbO	TiO_2	Bi_2O_3				
BX1	47.5	2.5	50	528	1.22×10^{-8}	0.51	0.294
BX2	45.0	5.0	50	613	4.43×10^{-8}	0.61	0.710
BX3	42.5	7.5	50	603	6.12×10^{-8}	0.69	0.659
BX4	40.0	10.0	50	538	7.64×10^{-8}	0.71	0.461
BX5	37.5	12.5	50	598	1.08×10^{-8}	0.74	0.357

Similarly, the dc-conductivity is also measured by applying 5V regulated dc-supply and using a microvoltmeter (Systronics 413, India) having input impedance 10 Mohm. While doing the calculation the effective value of resistance has been taken into consideration.

3. Theoretical considerations

Alternating current conductivity is very interesting. In every amorphous semiconductor, the frequency dependence of ac-conductivity follows the equation

$$\sigma(\omega) = A\omega^{s}, \tag{1}$$

where A is the constant, dependent on temperature and S is the frequency exponent, is near unity (≤ 1) and may be weakly temperature dependent.

Pike [10], Springett [16] and Elliott [11] have suggested that the ac-conductivity is a phenomenon due to hopping of charge carriers over the barrier, called HOB. HOB model discussed the temperature and frequency dependence of conductivity and the exponent S is determined from the relation

$$S = 1 - \frac{\sigma\, kT}{W}, \tag{2}$$

where W is the binding energy of the carrier in its localized site, which is assumed to be band gap, k is the Boltzman's constant. The values of S obtained from eq. (2) are the theoretical values.

When $N(E_F)$ is finite, the hopping transport of electrons occurs near Fermi level. Austin [17] and Mott and Davis [1] have suggested for single electron motion undergoing quantum mechanical tunnelling, the expression for ac-conductivity as

$$\sigma(\omega) = \frac{\pi}{3} e^2 kT \{N(E_F)\}^2 \alpha^{-5} \omega \left[\ln\left\{\frac{\nu_{ph}}{\omega}\right\}\right]^4, \tag{3}$$

where $\frac{\pi}{3}$ is the numerical constant, α is the electron wave function decay constant, ν_{ph} is the phonon frequency and $N(E_F)$ is the energy density of the states near Fermi level.

The hopping distance R at frequency ω is given by

$$R = \frac{1}{2\alpha} \ln\left[\frac{\nu_{ph}}{\omega}\right], \tag{4}$$

$$R = \frac{1}{2\alpha} \ln \frac{\nu_{ph}}{\omega\tau_0}$$

where τ_0 is the characteristics relaxation time. The frequency exponent S is given by

$$S = 1 - \tag{5}$$

Eq. (5) shows that, the exponent is dependent on frequency only and independent of temperature. Quantum mechanical tunnelling (QMT) of a carrier through the potential barrier between the sites separated by a distance R, demands that (i) ac-conductivity should be dependent on temperature and (ii) exponent (S) independent of frequency, whereas in hopping of charge carriers over the barriers (HOB) model demand, exponent (S) to be dependent on temperature.

In the present glass system, in the high temperature range ac-conductivity is dependent on temperature (Figure 3) and independent in lower temperature range.

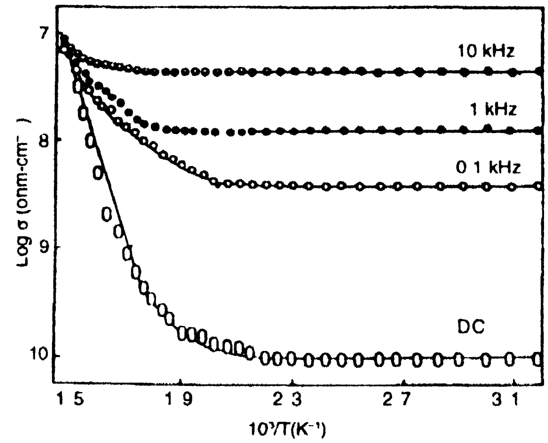

Figure 3. Plot of log $\sigma(\omega)$ *versus* $10^3/T$ for sample BX1 at different frequencies 0 1, 1 and 10kHz, BX1 - 47.5 PbO-2 5 TiO_2 - 50Bi_2O_3

Eq. (3) is derived by assuming that the multiple hopping is neglected means the hopping is considered only between independent pairs of charge centres and no correlation between hop energy and hopping distance.

However, Pollak [12] has replaced the numerical factor $\pi/3 = (1.047)$ in eq (3) by $\pi^3/96 = (0.322)$. Similarly, Butcher and Hyden [13] have replaced the same factor by 3.66 $\pi^2/6 = (6.020)$.

These values of numerical factor are different, but while plotting $\sigma(\omega)$ *versus* T, will not change the behaviour by the change in factor. However, this may affect the value of energy density of states $N(E_F)$ (Table 2). The theoretical discussion of

Table 2. Values of $N(E_F)$ at 10 kHz at 313 K from Mott and Davis [1], Pollak [12], Butcher and Hyden [13] formula

Sample	Glass composition (mol %)			$N(E_F) \times 1020$ (eV^{-1}-cm^{-1}) from the formula given by		
	PbO	TiO_2	Bi_2O_3	Mott and Davis	Pollak	Butcher and Hyden
BX1	47 5	2.5	50	2.538	5 393	1.058
BX2	45.0	5.0	50	2 595	4.675	1.082
BX3	42.5	7.5	50	2.927	5.273	1.221
BX4	40.0	10.0	50	1.073	1.933	0 441
BX5	37.5	12.5	50	1.284	2.313	0 535

hopping over the barrier (HOB) and quantum mechanical tunnelling (QMT) model has been reported. However, the QMT model is used to discuss the results of ac-conductivity in the present glasses.

4. Results and discussion

For amorphous materials various types of conduction mechanisms have been suggested :

i. Band conduction
ii. Conduction in localized states near band edge
iii. Conduction in localized states near Fermi level and
iv. Conduction in extended states.

The band conduction is generally observed in crystalline semiconductors. The conduction in localized states near band edge demands temperature dependence of ac-conductivity to be independent of frequency upto 10 MHz. Also for the transport by carriers excited to the extended states, we may expect that the $\sigma(\omega)$ should satisfy the Drude type formula.

$$\sigma(\omega) = \frac{\sigma_{dc}}{1+\omega^2\tau_0^2}, \tag{6}$$

where τ_0 is relaxation time, which is very short (10^{-15}s) and a decrease in $\sigma(\omega)$ with $1/\omega^2$ is not expected until a frequency of approximately 10^{15} Hz is reached. The conduction in localized states near Fermi level occurs when ac-conductivity is temperature independent and varies linearly with frequency. When $N(E_F)$ is finite the hopping transport by electrons occurs in localised state near Fermi level.

Plot of log of measured ac-conductivity log $\sigma(\omega)$ *versus* 10^3/T at different fixed frequencies for samples BX1 is shown in Figure 3. The behaviour is more or less similar to that reported for the different transition metal oxide phosphate glasses [6, 18]. At low temperature the conductivity shows weak temperature dependence – almost constant up to 501K and substantially higher than dc-conductivity (σ_{dc}). The value of $\sigma(\omega)$ is also higher for higher frequency. At higher temperature, the temperature dependence becomes strong and variation of $\sigma(\omega)$ with frequency is small. At still higher temperature the measured conductivities at all frequencies become equal and also equal to dc-conductivity. Similar type of temperature dependence has been observed in other samples BX2, BX3, BX4 and BX5. Therefore, these plots for other samples have not been given. The nature of curves in Figure 3 for dc and ac-conductivity is observed to be same.

Table 1 gives a summary of all the relevant parameters *i.e.* σ_{ac} at 533K, activation energy of dc-conduction at 533K and S_{expt} as obtained in the case of some of the typical glass compositions. The activation energy has been calculated from σ_{dc} *versus* 1/T plot, given by the expression

$$\sigma_{dc} = \sigma_{0\,\exp} - \left[\frac{\Delta E}{kT}\right] \tag{7}$$

The glass transition temperature (Tg) of the glasses is also mentioned in Table 1.

The DTA curves of all the glass samples are shown in Figure 2. Each curve exhibits an endothermic dip due to glass transition, and one or more exothermic peaks corresponding to crystallization or phase transition.

From the plot of log $\sigma(\omega)$ *versus* log 1/T (Figure 3) for sample BX1, it is observed that the ac-conductivity remains almost unchanged with temperature upto 501K. This suggest that the conduction occurs in localized states near Fermi level. The nature of the curve log $\sigma(\omega)$ *versus* 1/T up to 501K is temperature independent. At higher temperature, the value of $\sigma(\omega)$ starts increasing from the constant value and at still higher temperature it shows same value for different frequencies.

Plot of log $\sigma(\omega)$ *versus* log ω are shown in Figure 4 at temperature 543K for sample BX1, BX2, BX3,BX4, and BX5. At low temperature, the ac-conductivity obeys the relation $\sigma(\omega) = A\omega^s$. The value of exponent determined from the slopes of these plots (called experimental values) are reported in Table 1.

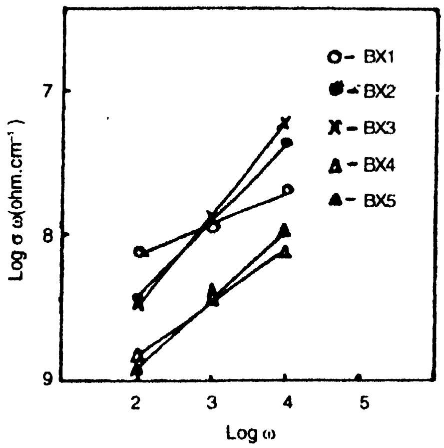

Figure 4. Plot of log $\sigma(\omega)$ *versus* log ω for samples BX1, BX2, BX3, BX4 and BX5 at temperature 543K.

Figure 5 shows plot of log σ_{dc} at temperature 473K *versus* hopping distance R. The value of α is determined from the

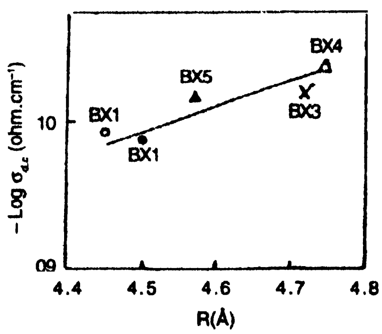

Figure 5. Plot of log σ_{dc} *versus* hopping distance R for four differen samples BX1, BX2, BX3, BX4 and BX5 at temperature 473K.

slope of this plot found to be equal to 0.90 $Å^{-1}$. This has been obtained from the relation

$$\sigma_{dc} \sim \text{constant} \exp(-2\alpha R). \quad (8)$$

The value of $N(E_F)$ calculated at 10 kHz at the temperature of 313K (taking electron wave function decay constant $\alpha = 0.09$ $Å^{-1}$) from Mott, Pollak and Butcher formula [1, 12, 13] reported in Table 2. The range of $N(E_F)$ is found to be 10^{20} $(eV)^{-1}cm^{-3}$ Such a value of $N(E_F)$ near the Fermi level suggests localized states. The value of α is calculated from the plot of log σ_{dc} *versus* hopping distance, R at 473K (Figure 5). The hopping distance, R has been calculated by the formula

$$R = \frac{M^{1/3}}{(Nod)^{1/3}} \quad (9)$$

where No is the Avogadro's number, M is the molecular weight of the glass sample and d is the density of glass sample.

In conclusion, it may be stated that the ac-conductivity increases with frequency. The value of $N(E_F)$ is finite for the hopping transport by electrons with energies 10 near the Fermi level. The exponent (S) in equation $\sigma(\omega) = A\omega^s$ is less than 1 for the frequencies at which ac-conductivity is measured, and is found to be independent of frequency. Also $\sigma(\omega)$ is proportional to temperature is the range 501-673 K and independent in the range 313-501K.

The values of $N(E_F)$ depends strongly on the value of ν_{ph}. The value of $N(E_F)$ is calculated using eq. (3) and considering the value of electron wave function decay constant (α) equal to 0.9 $Å^{-1}$. The numerical constants given by Mott and Davis (1), Pollak [12], Butcher and Hyden [13] have been used to evaluate the value of $N(E_F)$ and for comparison the data are presented in Table 2. In the light of above facts, it may be concluded that the hopping conduction occurs in localized state near Fermi level.

5. Conclusion

In the present glass system, it is found that dc and ac-conductivity $\sigma(\omega)$ vary linearly with temperature in high temperature region, and independent at lower temperature. Ac-conductivity follows the relation $\sigma(\omega) = A\omega^s$. Ac-conductivity follows linearity with frequency. The electron overlap integral decay constant (α) is found to be 0.9 $Å^{-1}$ The range of $N(E_f)$ is found to be 10^{20} $(eV)^{-1}$ cm^{-3}, suggesting conduction in localized states near Fermi level. Thus for the above reasons, the QMT model explains the results of ac-conductivity satisfactorily for the lead-bismuth-titanate glass system.

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References

[1] N F Mott and E A Davis *Electronic Processes in Non-Crystalline Materials*, 2nd edn (Oxford : Clarendon) (1979)

[2] M Sayer and A Mansingh *Phys. Rev* **B6** 4269 (1972)

[3] A Mansingh, J K Vaid and R P Tandon *J Phys* **C10** 4061 (1977)

[4] H K Rockstad *Solid State Commun* **7** 1507 (1969) ; *J Non Cryst Solids* **2** 224 (1970)

[5] H Segawa *J Phys Soc Jpn* **36** 1087 (1974)

[6] A Ghosh and B K Chaudhuri *J Mater Sci* **22** 2367 (1987)

[7] J T Polanco and G G Roberts *Phil Mag* **25** 117 (1972)

[8] Ledec'hx and J F Palmier *J. Non-Cryst Solids* **18** 265 (1975)

[9] D K Burghate, V S Deogaonkar (Miss) S V Pakade and S P Yawale *Indian J Pure Appl Phys* **33** 225 (1995)

[10] G E Pike *Phys Rev* **B6** 1572 (1972)

[11] S R Elliott *Phil Mag* **36** 1291 (1977)

[12] M Pollak *Phil Mag* **26** 519 (1971)

[13] P N Butcher and K J Hyden *Phil Mag* **36** 657 (1977)

[14] V G Kher and C S Adgaonkar *Indian J Pure Appl Phys* **110** 902 (1972)

[15] S P Yawale and S V Pakade *J Mater Sci.* **20** 5451 (1993)

[16] B R Springett *J Non-Cryst Solids* **15** 179 (1974)

[17] I G Austin and N F Mott *Adv Phys* **18** 41 (1969)

[18] A Mansingh, V K Davan and M Sayer *Phil. Mag.* **B48** 215 (1983)